Electric Double Layer at Polycrystalline Platinum-Electrolyte Interface Probed By Electrokinetic Streaming Current Method

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Abstract

Interfacial charging and ionic conductivity in the diffuse layer of polycrystalline platinum (poly-Pt)- non-adsorbing electrolyte interface was studied using a combined electrochemical-electrokinetic method. Assuming no specific adsorption of ions, electronic charge on the metal (metal charge) was found to increase monotonically for acidic, neutral, and basic pH, with applied potential up to 0.95 V vs SHE. Non-monotonic metal charging was not observed; however metal charge was found to saturate to a near constant positive value at higher applied potentials, possibly due to ion-crowding in the diffuse layer. With respect to the potential of zero free charge (PZFC) of Pt, the potential at which zeta potential was zero, was found to be lower in acidic pH, higher in basic pH, and almost equal in neutral pH. In addition, oxide coverage was calculated from cyclic voltammetry and H coverage was calculated from Frumkin adsorption isotherms. They were added to the metal charge to calculate the 'total charge', and was compared with the CO-displacement results for Pt(111) from literature. The results from these two methods showed good agreement, with the electrokinetic method being applicable for a larger potential window (V > 0.75 V). Ionic

conductivity in the diffuse layer was found to be minimum at applied potentials where zeta potential is 0, and its value was equal to the bulk ionic conductivity of the electrolyte. For all the other applied potentials, diffuse layer ionic conductivity was higher.

Introduction

An electric double layer (EDL) is formed at a solid-liquid interface due to the difference in chemical potential of ions and electrons in the two media. Knowledge about the structure of EDL at electrocatalyst-electrolyte interfaces is essential for proper modeling of electrochemical reactions, charge storage and ion adsorption properties in electrochemical systems, such as fuel cell, electrolyzers, electrochemical double layer capacitors, water desalination devices etc.[1–4] Electrodes used in the above-mentioned applications are porous in nature and contain micro and mesopores. Because of the small size and complex geometry of the pores, EDLs from catalyst and support particles overlap, and give rise to some transport and reaction kinetics properties that are not observed in 2D electrodes studied in traditional electrochemical experiments.[5–7] The EDL formed at the Pt-electrolyte interface is frequently studied in the electrochemistry community as Pt group metals (PGM) and their alloys are most active for hydrogen oxidation (HOR) and oxygen reduction reactions (ORR).[8,9] Potential of zero charge (PZC), defined by Frumkin to explain the charging behavior of metals in contact with an electrolyte is a crucial parameter in determining electrocatalytic properties. It is defined as the potential at which a metal in contact with an electrolyte carries zero charge. For ideal polarizable metals, such as Hg, PZC can be directly determined from the minimum of the applied potential vs differential capacitance curve obtained from electrocapillarity experiments.[10] For these interfaces, charging is mostly electronic (metal charge). However, for highly reactive metals like Pt, electrosorption of ions from the electrolyte

and other Faradaic reactions can dominate over metal charging. Huang et al. have shown a comparison of metal charge and charge transferred due to Faradaic reactions on Pt, and the former is an order of magnitude lower.[11] As a result, it is difficult to determine the PZC of Pt directly from electrochemical experiments. There are three related physical quantities that become important regarding the discussion of PZC[12]: work function of the metal, the potential of zero free charge (PZFC) and the potential of zero total charge (PZTC). Work function is the potential required to ionize the metal in vacuum environment, and as a result, is less relevant for metal-electrolyte interfaces. PZFC is associated with electronic charging (also called metal-charging) of the metal at a metal-electrolyte interface and is defined as the applied potential at which the electronic charge on the metal is 0. It is not possible to directly measure PZFC for highly reactive metals like Pt solely by using electrochemical experiments. Electrochemical techniques are only sensitive to Faradaic charge transfer between the electrode and electrolyte, which can occur due to both electronic charging of the metal as well as charging due to electrosorption of different chemical species on the Pt surface. Cyclic voltammetry (CV) reveals that perchlorate (ClO_4^-) anions are the least adsorbing on Pt surface. When CV is performed in perchlorate anion containing electrolyte with small concentrations of SO_4^{2-}, Cl^- etc., in addition to the background current found in perchlorate containing electrolytes, currents due to electrosorption of these anions are observed.[13–15] CV studies of Pt in aqueous electrolytes reveal that H_{ad}, OH_{ad} and O_{ad} are electrosorbed on the Pt surface even in the perchlorate containing electrolytes. When potential is applied on Pt, the measured current can be sub-divided into metal charging current and current due to electrosorption. The measured current can be integrated with respect to time to compute charge transferred between the metal and the electrolyte. Charge computed in this way, defined as 'total charge', is the sum of metal charge and the charge transferred due to electrosorption of chemical

species on the metal surface that exist in the form of electric dipoles. Alternatively, it is possible to integrate the transient current-time curves using CO displacement method, where CO is introduced under constant applied potential, and it displaces adsorbed positive or negative charge on the surface. PZTC is the value of the applied potential at which this 'total charge' is 0. Thus, one can only measure the PZTC of Pt using electrochemical techniques like CO displacement or integrating current from the CV.[16,17] Assuming a constant double layer capacitance, PZFC can be extrapolated from PZTC.[18] This approximation is neither thermodynamic nor very rigorous, as it well-known that differential capacitance shows a local maximum near PZFC due to the reorientation of water dipoles.[19] However, an approximation of some kind is necessary to estimate PZFC as it is not directly measurable. A good discussion on the conceptual difference between PZFC and PZTC for PGMs is provided in the review article by Climent and Feliu.[20] Using CO displacement, PZTC of poly-Pt has been directly measured to be ~ 0.3 V vs RHE for pH 1 in non-adsorbing electrolyte.[17,21] From CO displacement experiments, PZTC for Pt(111) was also found to be ~ 0.3 V vs SHE at pH 1.[18] From the measured value of PZTC of Pt(111), the PZFC was calculated using the EDL parameters known for Pt(111), to be at 0.28 V vs. SHE and is independent of pH.[18] Even though the measurement of PZFC is quite difficult and cannot be directly done by electrochemical techniques, it is very important for the purpose of EDL modeling and fundamental understanding of the interface. For this reason, non-electrochemical methods must be used to experimentally determine PZFC. In the past, potential dependent orientation of water dipoles inferred from laser-pulse experiments was used to estimate the PZFC at single crystal Pt-electrolyte interface.[22] Non-linear optical techniques like sum-frequency generation (SFG) was applied to poly-Au under applied potential. SFG revealed the location of PZC of Au quite accurately by observing the orientation of interfacial water dipoles.[23] At potential lower than PZC,

the OH^- of adsorbed water pointed away from the electrode while H^+ pointed towards it. SFG signal in this case was strong. When the potential was increased to PZC, the signal decreased, implying random orientation of water dipoles. The signal strength increased again on further increase of the potential. The process of determining PZFC of Pt from second-harmonic generation (SHG) is still under development.[24]

When no potential is applied on the metal externally (e.g., using a potentiostat), then charging at the interface takes place via formation of surface complexes mediated by ions in the electrolyte. This is known as site-binding equilibria[25] and is a universal theoretical framework used to explain how the surface charge on solids changes with solution pH or concentration of specifically adsorbing ions. Generally, charge on the solid decreases with increasing pH.[26] The value of pH at which the electrokinetic properties (e.g., zeta potential) becomes 0 is called the 'iso-electric point (IEP)'. If the solution contains no specifically adsorbing ions or functional groups, then charging occurs mainly via protonation/deprotonation and is determined by pH of the solution. The value of pH at which this charge becomes 0 is called the zero net-proton charge and is measured by potentiometric titration. Point of zero charge is the umbrella term used to indicate any of the above-mentioned cases.[27] When electrode charging is controlled via potentiostat as well as pH of the electrolyte, all these parameters (PZFC, PZTC and IEP) become relevant physical quantities[28]. In this manuscript, unless otherwise stated, PZC refers to potential of zero charge (related to the applied potential), and not point of zero charge.

Typically, electronic charge at a metal-electrolyte interface (metal-charge) monotonically increases with applied potential. As a result, it is assumed that there is only one PZFC for a metal with specific crystalline structure. However, Frumkin and Petrii in their seminal work in 1975[12], highlighted the works of Kolotyrkina et al.[29] and Balashova and Frumkin[30], where using

radiotracer as well as electrokinetic techniques, the authors observed a second PZC at a higher applied potential of 0.75 – 0.8 V vs. NHE for Pt. They claimed this PZC to be PZFC. These works are frequently referred in literature as pioneering works where metal-charge reversal was observed for the first time. However, very little was said about the experimental conditions that were used in these studies. Kolotyrkina et al. used the radiotracer method to measure sodium and sulfate adsorption onto the disk of Pt at pH 6 and in the Na_2SO_4 electrolyte.[29] They showed two PZC values- 0.13 and 0.47 V (vs. NHE). Balashova and Frumkin observed deflection of a thin Pt wire under electric field of 40 V/cm.[30] The wire was stretched on one end by a glass bead and the potential of the wire was changed by purging the solution with various mixtures of oxygen in argon. Displacement of the wire was measured using a microscope. The potential where the direction of displacement changes indicates the PZC. Their experiments were conducted in poisoning electrolytes $2 \times 10^{-5} N$ HCl and $2 \times 10^{-5} N$ H_2SO_4, where adsorption of Cl^-, SO_4^- and HSO_4^- on Pt cannot be neglected. As a result, Balashova et al. most likely measured the net charge on the Pt electrode, which is the sum of metal charge and that due to specific adsorption of anions mentioned above. At high applied potentials, specific adsorption of anions like Cl^-, SO_4^- etc. on Pt is significant.[13,31,32] Specific adsorption of negatively charged ions may make the net charge on the electrode negative, even though the electronic charge on the metal is positive. Our previous study on polycrystalline gold (poly-Au) - KCl interface revealed this phenomenon. It was found that the net charge on poly-Au electrode in non-adsorbing $KClO_4$ electrolyte was positive around 700 mV vs SHE, whereas it was negative in adsorbing KCl electrolyte at the same pH and nearly the same applied potential.[33] The applied potential is above the known range of PZFC for Au.[34] This phenomenon, also known as 'overcharging', 'charge inversion' or 'overscreening', which essentially means an excess of counterions in the compact layer, has been found at many solid-

liquid interfaces, e.g., electrolytes containing multivalent ions, charged polymers etc. Lyklema's review article contains a detailed account of this phenomenon in colloidal systems.[35] It has also been predicted to occur in ionic liquids.[36,37] This phenomenon may occur due to formation of chemical bonds as well as strong ion-ion correlation in EDL. Whatever the physical origin of overcharging, at a metal-adsorbing electrolyte interface, even if the applied potential is above PZFC, the net charge on the electrode may become negative due to specific adsorption of anions on the electrode. One may erroneously interpret it as a second PZFC or a metal-charge-reversal. The experiments by Balashova et al. in adsorbing electrolytes showed charge reversal at high applied potentials at ~0.8 V vs. NHE. What Balashova et al. inferred as the metal-charge-reversal might actually be the net-charge-reversal. However, in a completely independent study, Feliu's group used a different technique- laser induced orientation of adsorbed water dipoles to investigate interfacial charging of Pt single crystal electrodes. Their results point towards the possible, yet not confirmed, existence of a second PZFC.[22] Motivated by these experiments, Huang et al. recently used a modeling approach to explain the non-monotonic metal charging behavior of Pt(111)-electrolyte interface.[11] According to the prediction of the model, metal charge increases with applied potential up to a certain value, then decreases and reverses its sign.

One convenient method of measuring charge on the metal is by measuring charge in the diffuse layer, as these two quantities are connected by electroneutrality equation in the EDL. Electrokinetic streaming current technique can be applied to measure potential at the slip plane (zeta potential). It is usually assumed that slip plane coincides with the OHP[38], however, some models assume it to be inside the diffuse layer[39]. For this study, we will consider it to coincide with OHP. Charge in the diffuse layer can be calculated from the measured OHP potential. Net charge on the metal is the sum of metal charge and charge due to specific adsorption of ions at

IHP. When specific adsorption of ions is not significant, electrokinetic methods provide a fair estimate of electronic charge on metals. Frumkin in his seminal book "Potential of zero charge" qualitatively explains the correlation between PZFC and zeta potential.[40] When specific adsorption of ions is not significant, PZFC should ideally be equal to the potential at which zeta potential is zero. Hence, electrokinetic methods can be used to determine PZFC of metals. Electrokinetic methods have significantly advanced in precision from when Frumkin and collaborators used these techniques, yet no attempt has been made to prove or disprove their claims of metal-charge reversal. Our earlier works presented a novel method to integrate an electrochemical three-electrode setup with a traditional electrokinetic set-up to apply potential on poly-Au surface, and measure zeta potential as well as charge in the diffuse layer at the metal-electrolyte interface.[33,41] Measured zeta potentials for various applied potentials were found to be in a good agreement with the non-electrokinetic methods, such as atomic force microscopy (AFM) studies.[33,42,43] The method correlated the known range of PZC of poly-Au with the applied potential at which zeta potential was found to be zero. As mentioned earlier, it was observed that even at potentials higher than PZFC, net charge on the metal was negative due to the specific adsorption of Cl^- ions on the metal. Zeta potential was found to reverse its sign and become negative when Cl^- adsorbed on strongly on the surface.[33]

In this study, we use the combined electrokinetic-electrochemical method developed by us to study interfacial charging, PZFC, PZTC, and ionic conductivity in the diffuse layer at poly-Pt-electrolyte interface. This is the first experimental work following Frumkin's earlier studies that attempts to answer the question of the non-monotonic charging of poly-Pt at high applied potentials using electrokinetic method. The electrolyte $KClO_4$ was chosen as ClO_4^- is known to be the least adsorbing anion for Pt.[13,14] CVs were used to complement the electrokinetic experiment

by estimating oxide coverage on Pt. This work shows an attempt to answer some of the most fundamental questions of the EDLs at poly-Pt electrolyte interface using old but significantly improved method.

Theoretical considerations

The method of calculating zeta potential (ζ) from streaming current at the metal-electrolyte interface, and subsequent analysis using Poisson-Boltzmann distribution to calculate net charge on the electrode was discussed in our previous studies.[33,41] In this study, we only provide a summary of the process and the most important equations to determine interfacial charges and ionic conductivities. Details of the experimental method are discussed in Supplementary Materials SM sections S1 and S2. Section S1 outlines the procedure and experimental details to measure ζ when no potential is applied on the electrode, i.e., when the electrode is in open-circuit voltage (OCV) condition. This is the standard procedure for measuring streaming current. Section S2 contains the detailed step-by-step description and experimental parameters to determine ζ when potential is applied on the electrode by a potentiostat.

Two pieces of thin electrochemically clean poly-Pt electrodes were mounted symmetrically inside a microchannel. Potential V_{app} was applied on the electrodes with respect to a reference electrode (RE) in an external beaker containing the electrolyte. At the same time, the electrolyte was flown through the microchannel at near-constant pressure P. The resultant current I_{tot} was measured by a counter-electrode (CE) located in the same beaker containing the RE. I_{tot} consists of two parts:

$$I_{tot}(V_{app}, P) = I_{bulk}(V_{app}) + I_S\left(P, \zeta(V_{app})\right) \quad (1)$$

Where, I_{bulk} is the bulk current due to the applied potential V_{app} on the metal and I_S is the streaming current due to the transport of ions in the diffuse layer. I_{bulk} is electrochemical in nature and arises due to the applied potential. This is the current one would measure in a chronoamperometry experiment if potential V_{app} is applied. I_S depends on ζ, which in turn depends on V_{app}. From Eq. (1), ζ can be calculated using a modified version of Helmholtz-Smoluchowski equation[44]:

$$\zeta = \frac{\eta}{\epsilon_r \epsilon_0} \frac{L}{A} \frac{dI_S}{dP} = \frac{\eta}{\epsilon_r \epsilon_0} \frac{L}{A} \frac{dI_{tot}}{dP} \tag{2}$$

where, the first equality is the modified Helmholtz-Smoluchowski equation. The second equality is introduced in our earlier work[33], as I_{tot} is the experimentally measured current, and the P dependence of I_{tot} is only introduced through I_S. In Eqn. (2), L is the length of the microchannel, A is the cross-sectional area of the channel, η is the viscosity of the electrolyte and ϵ_r is the dielectric constant of the electrolyte. For sufficiently dilute electrolytes, η and ϵ_r are usually approximated to be equal to those of water. The experimental parameters (L, A etc. are discussed in SM section S1). The charge density in the diffuse layer, σ_d, can be calculated from Poisson-Boltzmann distribution. For a binary symmetric (z:z) electrolyte, it takes the analytical form:

$$\sigma_d = -(8RT\epsilon_r \epsilon_0 c^{bulk})^{\frac{1}{2}} \sinh\left(\frac{ze\zeta}{2k_B T}\right) \tag{3}$$

where, c^{bulk} is the bulk concentration of the electrolyte and z is the valency of the cation or anion. It is assumed that the bulk concentration of cation or anion is greater than that can arise from the variation of H^+ or OH^- ions due to the change of pH. This condition is not strictly maintained in all the experimental conditions encountered in electrokinetics but is true for this study. Here, c^{bulk} = 0.1 M, whereas 1 < pH < 12. Ionic conductivity, κ^{OHP} near OHP in the diffuse layer can be approximated as[33,41]:

$$\kappa^{OHP} = \frac{F^2 z^2}{RT} \sum_i D_i c_i^{bulk} exp\left(-\frac{ez\zeta}{k_B T}\right) \quad (4)$$

where, D_i and c_i^{bulk} are diffusion constant and the bulk concentration of the i^{th} ion. D_i in diffuse layer is approximated to be the same as that in bulk, which cannot be generally true, as for example, in the case of ion-crowding in the diffuse layer. Eqn. (5) is valid for binary (z:z) electrolytes, which is true for this study (z=1). F is the Faraday constant and R is the universal gas constant. All measurements were done at room temperature (T=300 K).

At the Pt-electrode interface, electrosorption of H_{ad}, OH_{ad} and O_{ad} occurs as is known from CV and XPS.[20,45] The electrosorbed species can be conceptualized as surface dipoles, where the metal and the adsorbed species contain fractional electronic charges.[46,47] The next layer in the EDL is inner Helmholtz plane (IHP) and it is mostly populated with adsorbed water dipoles (H_2O_{ad}) in the absence of specific adsorption of ions. For Pt surface, ClO_4^- containing electrolytes are widely used because ClO_4^- is the least adsorbing anion[13,14,48]. The plane outside of IHP is the outer Helmholtz plane (OHP), which is the plane of closest approach by solvated ions. Potential at the OHP under certain electrolyte conditions (10^{-5} M and higher[49]) coincides with the potential at the slip plane in electrokinetic measurements, known as zeta potential (ζ). At and beyond the OHP in the diffuse layer the ions are hydrodynamically mobile. The schematic of the EDLs is shown in SM Figure S6.

Electroneutrality in the EDL constrains the charge in diffuse layer by:

$$\sigma_M + \sigma_{IHP} + \sigma_d = 0 \quad (5)$$

where, σ_M is the metal charge and σ_{IHP} is the charge of specifically adsorbed ions at the IHP. If experiments are performed in the least adsorbing electrolyte, it is usually assumed that the

IHP does not contain ions and is mostly occupied by adsorbed water dipoles oriented according to the local electric field. Using the least adsorbing electrolyte (ClO_4^- containing electrolyte) for Pt, σ_{IHP} is assumed to be 0. Duval et al[28,50] modeled the charging of poly-Au electrode by assuming that there can be charges in surface oxides in the form of surface complexes like MOH_2^+ and MO^-, where 'M' is the metal. This charging is often called ionic charging as it is determined by the bulk concentration of H^+ and OH^- ions.[25] This charging mechanism can qualitatively explain the variation of ζ with pH of the solution when V_{app} is kept constant. The variation of ζ with pH at constant V_{app} may also arise from a pH dependent specific adsorption of ions at the IHP. Surface complexation models work very well for solid surfaces without electronic (potentiostatic) charging, and can explain the variation of charge at metal oxide-electrolyte interface due to change in pH.[25] The validity of surface complexation models has not been established for metal-electrolyte interfaces where electronic charging is also present. For the sake of computational simplicity, their contribution to interfacial charging will not be considered in this study.

Metal charge, σ_M obtained from this method ($\sigma_M \sim - \sigma_d$) can be combined with coverages of electrosorbed H and surface metal oxides to calculate 'total charge' (σ_{tot}). At Pt-electrolyte interface, when H^+ and OH^- are the only charge determining ions, σ_{tot} can be defined as:

$$\sigma_{tot} = \sigma_M - e\Gamma_H + e\Gamma_{OH} + 2e\Gamma_O \quad (6)$$

where, Γ_H, Γ_{OH}, and Γ_O are the surface density of dipoles corresponding to electrosorbed H_{ad} and surface oxide species (OH_{ad} and O_{ad}) respectively. A detailed discussion on the conceptual difference between σ_M and σ_{tot}, and hence PZFC and PZTC, is provided in Supplementary Materials section S6. The nature of electrosorbed species, a schematic diagram of the EDL containing them with potential drops across different layers are also discussed in the same section. The surface charge density σ, defined this way, has the unit coulomb per unit area. Γ has the unit

of area^{-1}. This relation was first proposed by Frumkin and Petrii from thermodynamic considerations[12] and later used for CO displacement experiments by Feliu and co-workers.[20] In Eqn. (6), it is assumed that there is no ion adsorption from the background electrolyte. For example, if sulfate (SO_4^{2-}) and bisulfate (HSO_4^-) containing electrolyte is used in the study, then they will also contribute to σ_{tot}. These ions are known to strongly adsorb on Pt.[13,31] When CO is introduced into the electrolyte, it replaces H and surface oxides and hydroxides according to the following reactions:

$$Pt - H_{ad} + CO \rightleftharpoons Pt - CO + H^+ + e^-$$

$$Pt - OH_{ad} + CO + e^- \rightleftharpoons Pt - CO + OH^- \quad (7)$$

$$Pt - O_{ad} + CO + 2e^- \rightleftharpoons Pt - CO + O^{2-}$$

CO displacement is usually done in potentiostatic conditions. As a result of the reactions in Eqn. (7), one measures σ_{tot} as shown in Eqn. (6). Although experimentally different, integrating current from the CV to get the charge is also affected by surfaces dipole concentrations. In capacitive potential window (~ 0.4-0.6 V vs RHE in pH 1 electrolyte) H, OH and O adsorptions are minimal and $\sigma_{tot} \sim \sigma_M$, as the latter two terms in Eqn. (6) are approximately 0. This is the reason why electrochemical techniques give a direct estimation of PZTC (V_{app} where $\sigma_{tot} = 0$). One can estimate PZFC (V_{app} where $\sigma_M = 0$)from Eqn. (6) by estimating Γ_H and Γ_{Ox} from CV or in-situ XPS.[45] The advantage of electrokinetic method is that it can directly estimate PZFC. Assuming $\sigma_{IHP} = 0$, PZFC is equal to V_{app} where ζ=0.

As mentioned in the Introduction section, the non-monotonic metal charging behavior at Pt(111)-electrolyte interface has been modeled by Huang et al.[11], and according to the model, σ_M increases with V_{app} for a certain range, then decreases with increasing V_{app}, and becomes negative.

In other words, there exists two PZFC values and one PZTC value for Pt-electrolyte interface. Figure 1 shows a schematic of studying metal charge reversal from electrokinetic ζ measurements. Essentially, if $\zeta(V_{app})$ is obtained for increasing V_{app}, one would observe, from Eqn. (3) and (5), that ζ first increases from negative to positive value, then it decreases and becomes negative. The V_{app} where $\zeta = 0$ for the 2nd time should be treated as the 2nd PZFC.

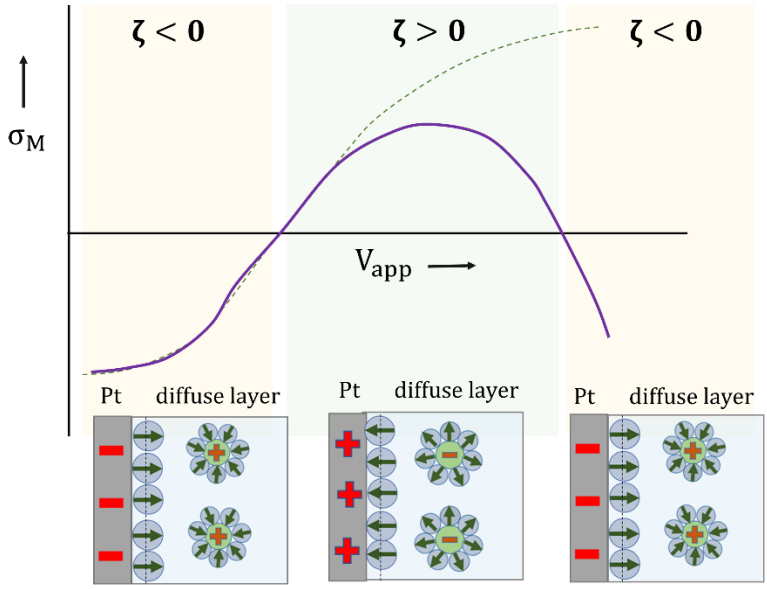

Figure 1: A schematic of non-monotonic metal charging behavior (metal-charge reversal), and its experimental signature in observed ζ. The dashed line shows the conventional monotonic metal-charging behavior.

Experimental

ASTM I (resistivity 18.2 MOhm-cm, 2 ppb total organic carbon (TOC)) grade deionized (DI) water, by Milli-Q Direct (Millipore Sigma) was used to prepare the solutions and cleaning of Pt surfaces. A 99.99 %, 0.5 mm thick poly-Pt foil (Sigma Aldrich, USA) was used as the sample

and the working electrode (WE). Extensive cleaning of poly-Pt was performed. First, poly-Pt foil was mechanically polished with alumina slurry of 5 μm, 3 μm and 0.05 μm in succession. Then, the foil was ultrasonicated for one minute in DI water. It was then flame annealed for one minute to vaporize the organic impurities. After that, poly-Pt was ultrasonicated again for one minute in a DI water. Cyclic voltammetry (CV) was used to clean the foil in 0.1 M $HClO_4$ solution between 0 to 1.2 V (RHE) at 350 mV/s for 20 cycles. Maximum precaution was taken to keep the samples as flat and clean as possible. Pt samples were connected to the sample holders inside the microchannel by double-sided tape. To connect the Pt samples with the WE clip of the potentiostat, copper wires were inserted on the back side of Pt (not in contact with electrolyte). Copper wires were connected to the Pt foils by electrically conductive epoxy (50% Ag and 50% resin). The electrical resistance between the Copper wire end and the Pt foil was checked with a multimeter, and was found to be less than 10 Ω, implying a good electrical connection.

$KClO_4$ was used as the background electrolyte (Sigma Aldrich, ACS reagent >99.0%). When no potential was applied and ζ was measured for different pH, both 0.001 and 0.1 M electrolyte concentrations were used. When potential was applied and streaming current was measured, 0.1 M electrolyte was used to decrease the uncompensated electrolyte resistance R_u in the setup. For titration, concentrated $HClO_4$ and KOH (Sigma Aldrich) were used. The pH in the external beaker, where the CE and RE were kept, was measured by an Ag/AgCl based pH sensor provided by Anton Paar. The details of pH measurement are provided in Supplementary Materials section S1 and S2. Ultra-high purity N_2 gas (Airgas NI-UHP 300) was bubbled for 5 mins before every measurement to purge O_2 and other dissolved gases in the electrolyte. N_2 bubbling was stopped before doing the streaming current measurements because the gas outlet was close to the CE.

The electrokinetic set-up used in this study was described in our earlier publication on Au electrode.[33] The microchannel consists of a rectangular channel where 2 cm x 1 cm poly-Pt samples were mounted symmetrically (separated by ~140 μm). The walls of the microchannel were made with polyether ether ketone (PEEK) for its high chemical resistance. Channel dimensions did not change from our earlier studies[33,41]. The separation between two Pt samples was set so that there is no electrical short between them. SM section S1 contains more details. The SurPASS 3.0, (Anton Paar, Graz, Austria) instrument was used to control the electrolyte pressure and flow rate. To calculate ζ of Pt without any applied potential (i.e., in OCV condition), streaming current was measured by the built-in Au electrodes inside the setup. The electrolyte was driven by pressure continuously changing from 800-200 mbar, and ζ was calculated from the slope of streaming current vs pressure. Data analysis was done by the Anton-Paar software. On the other hand, to measure ζ for different applied potentials, Ag/AgCl (9.5 mm outer diameter, Pine Research, NC, USA) was used as the reference electrode RE. To measure streaming current in this case, a coiled polycrystalline Platinum wire (6.5 mm OD, Pine Research, NC, USA) was used as the CE. Both RE and CE were in external beakers. During these measurements, pressure was kept nearly constant at 200, 400, 600 and 800 mbar. For pressure higher than 800 mbar, the time of liquid flow was found to be too low for accurate measurement of current. Details of the procedure and data analysis are explained in SM Section S2. Gamry 1010E (Gamry Instruments, PA, USA) potentiostat was used to apply potential and measure the total current. For CV analysis, Hydroflex reversible hydrogen electrode (RHE) made by Gaskatel, Germany was used.

For electrophoretic light scattering (ELS) ζ measurement of Pt particles, > 99.9% pure high surface area poly-Pt powder was used. The manufacturer reported surface area was 45 to 52 m^2/g and average particle size was 5 to 7.5 nm (Part number: 590079, Fuel Cell Store). It was cleaned

multiple times in ASTM I water by ultrasonicating for 20 mins. After that, the colloidal suspension was put in 0.001 M KCl and $KClO_4$ electrolytes (both 0.001 and 0.1 M), and ultrasonicated for 15 mins to obtain uniform dispersions. During the ELS measurements, these dispersions were continuously stirred to prevent agglomeration of Pt particles. For ELS ζ measurement, a nanoparticle analyzer (Horiba SZ-100) was used. The analyzer applies ±3V between two graphite electrodes to accelerate the charged particles in the dispersion. Laser of 532 nm wavelength was used to measure the electrophoretic mobility from which ζ was calculated by Smoluchowski equation.

Results and Discussion

Zeta potential (ζ) and diffuse layer charge (σ_d) of electrochemically clean poly-Pt surface without applied potential are plotted as functions of pH and are shown in Figure 2(a) and Figure 2(b) respectively. As no Faradaic charge transfer took place, the electrodes were in open-circuit voltage (OCV) condition during these measurements. The detailed method of extracting zeta potential from streaming current measurements was reported in our earlier work[33,41]. These plots are used as a baseline to compare with ζ for poly-Pt polarized by applied potential. ζ was calculated using Eqn. (2) from the measured $I_S(P)$ data. Figure 2(a) shows that for 0.001 M $KClO_4$, ζ changed from 16.5 mV at pH 3.2 to -63 mV at pH 10. For 0.1 M $KClO_4$, ζ changed from 35.6 mV at pH 2 to -79.8 mV at pH 12. For 0.001 M electrolyte, $3 < pH < 11$ because the bulk ionic concentration cannot deviate too much from 0.001 M. Following the same argument for 0.1 M, $1 < pH < 13$ which was already maintained. ζ(pH) trends and values are very similar for both 0.001 M and 0.1 M electrolytes. The general trend of ζ is to decrease and σ_d is to increase with increasing pH. This phenomenon is explained in electrokinetics community by a general site-binding model.[25] In low

pH electrolyte, protonation on the metal surface causes it to acquire positive charge. Negatively charged hydroxide and ClO_4^- ions in the diffuse layer balance the positive charge on the electrode, which implies $\zeta > 0$ from Eqn. (3). As pH increases deprotonation causes the metal to acquire negative charge. Positive ions (H^+ and K^+) will be present in the diffuse layer to shield this negative charge on the electrode, implying $\zeta < 0$ from Eqn. (3). In our previous study with Au-electrolyte interface, we gave a qualitative explanation, using the site-binding model why ζ decreases with increasing pH.[33]

A comparison of ζ(pH) for poly-Pt measured using the streaming current method with the traditional electrophoretic light scattering (ELS) method is provided in the SM Section S4. Both methods show isoelectric point (pH at which zeta potential is zero) in the range of pH 5-6 and agree well in the low pH region. However, at high pH region (pH > 6) the streaming current experiment shows increasing magnitude of ζ, reaching -63 mV at pH 10, whereas the ELS method shows less steep decline of zeta potential magnitude with pH, reaching -28 mV at pH 10 for 0.001 M $KClO_4$. This difference in zeta potentials might be due to the flame-annealing of the poly-Pt foil. Pt nanoparticles for ELS study were cleaned with DI water and sonicated but not subjected to flame annealing. Surface treatment is extremely important for ζ measurements. It is possible that due to flame annealing, more atomic sites on Pt foil were active for hydroxide adsorption and acquired a higher surface charge. In our earlier work, very good agreement was observed between ELS and streaming current measurements of ζ for poly-Au. In that study, both surfaces were subjected to the same cleaning protocols (oxidizing organic impurities with Piranha solution). In addition to surface pretreatment, surface wettability is also known to affect zeta potential.[51] The IEP of oxidized poly Au was found to be approximately 6. When no or minimum surface oxide is present, the IEP of poly-Au is close to 4.[52]

Figure 2(b) shows that σ_d varied from -0.12 μC/cm^2 to 0.57 μC/cm^2 for 0.001 M $KClO_4$ and σ_d varied between -2.75 μC/cm^2 to 8.21 μC/cm^2 for 0.1 M $KClO_4$. In Figure 2(b), σ_d is seen to be higher for 0.1 M electrolyte than that in 0.001 M concentration of the same electrolyte. If H^+ and OH^- are the principal potential determining ions (assumed to be the case for perchlorate anions as they are the least adsorbing on Pt), then σ_d should depend on pH and not on the concentration of the electrolyte. In that case, ζ(pH) should decrease with increasing electrolyte concentration. In absence of specific adsorption of ions, this is the general trend found at solid-electrolyte interfaces.[38] Contrary to the general trend, we measured very similar ζ(pH) for both 0.1 and 0.001 M electrolyte in Figure 2(a). At 0.1 M electrolyte concentration, the measured ζ of -75 mV at pH ~ 12 is quite high. Such high values of ζ in 0.1 M electrolyte is rarely measured by ELS. But there are reasons to doubt the zeta potential measurements using ELS too. Anomalous surface conduction, which can occur in ELS but not significant in streaming current measurements, can give a lower estimate of zeta potential in ELS.[53] Moreover, traditional electrophoresis fails to measure very high values of zeta potential because of a reason explained by O'Brien and White.[54] In electrophoresis, the charged colloidal particles are accelerated in the electric field applied between two electrodes in the solution. For higher ζ, charge in the diffuse layer is higher and consequently, force on the counterions which is opposite in direction to the force on the particle, is also higher. This backward force slows down the particle and the estimated ζ is lower than the true value. This limitation is not present in electroacoustics. Hunter et al. could measure ζ of polystyrene sulfate latex beads in 0.1 M KCl up to ~66 mV using electroacoustics.[55] In conclusion, the discrepancy in the magnitude of ζ observed in streaming current and ELS measurements may come from inherent experimental limitations of ELS and the surface pretreatment procedures.

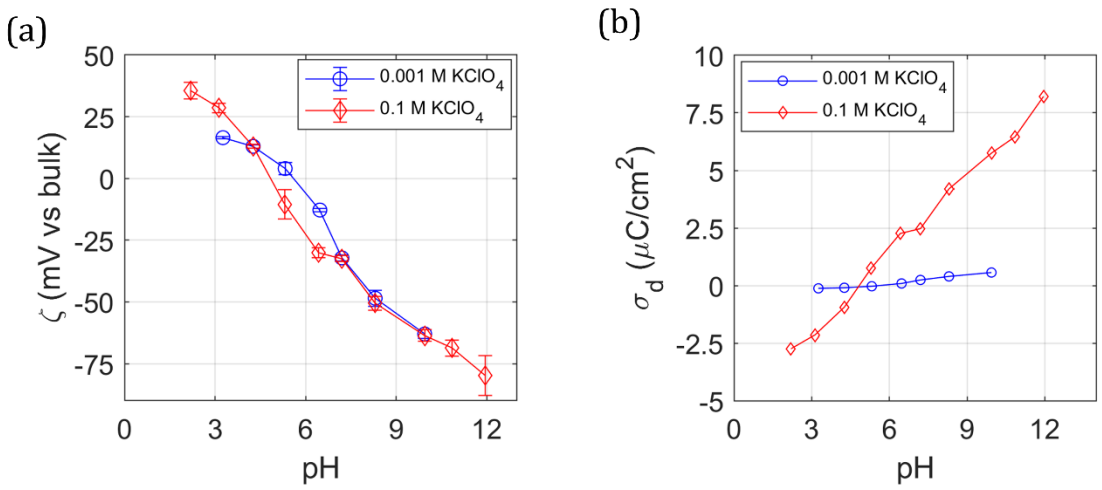

Figure 2: (a) ζ as a function of pH calculated from streaming current, I_S, and (b) $\sigma_d(pH)$ for poly-Pt-electrolyte interface. No potential was applied on the poly-Pt sample (OCV condition).

ζ as a function of applied potential for poly-Pt-electrolyte interface for 3 pH values (acidic, neutral, and basic) is plotted in Figure 3. Potential V_{app} was applied on Pt with respect to Ag/AgCl RE, but it was converted to SHE before plotting it in Figure 3. It was done to conform with literature convention as PZC for Pt is usually reported either vs SHE or RHE. Potential at RHE with respect to SHE is affected by solution pH. As measurements were done at different pH values, SHE is a more convenient choice. PZFC (0.28 V vs SHE[18] for Pt(111)), which is independent of pH is plotted as a vertical line for reference. Figure 3(a) shows that ζ increases with increasing V_{app} for any constant pH. It shows nearly linear trend with applied potential for pH 7 and 12. For pH 2, ζ increases almost linearly with V_{app} until 0.63 V vs SHE and then it asymptotically approaches 90 mV for V_{app} > 0.7 V vs SHE. This increase in zeta potential with applied potential is due to the fact that σ_M increases with increasing V_{app}. Assuming σ_{IHP} does not change appreciably with V_{app} (no specific adsorption), then σ_d should decrease to maintain the overall

electroneutrality in the EDL (Eqn. (5)). This is confirmed by Figure 3(b), where σ_d decreases monotonically for all three pH for poly-Pt as applied potential is increased. As an example, for pH 2 it decreased from 2.7 μC/cm^2 at V_{app}= 0.04 V vs SHE to -10.6 μC/cm^2 at V_{app}= 0.96 V vs SHE. Overall, good agreement was observed between the data in Figures 2(a) and 3(a), and the details of how to compare these data sets are shown in SM Section S5.

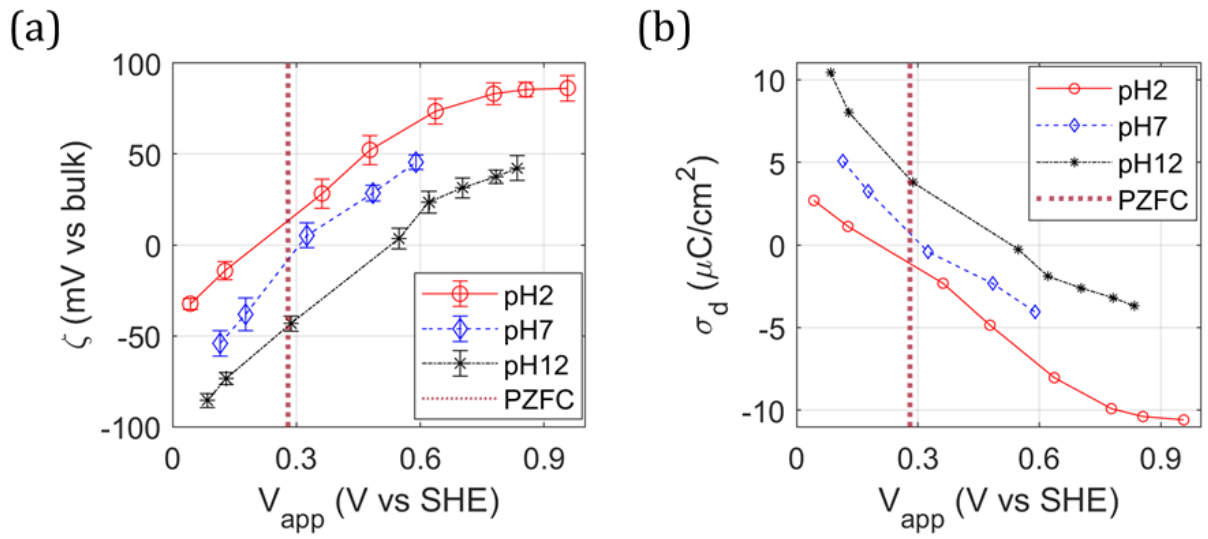

Figure 3: (a) $\zeta(V_{app})$ and (b) $\sigma_d(V_{app})$ of poly-Pt in 0.1 M $KClO_4$ for acidic, neutral, and basic pH. Value of PZFC (0.28 V vs SHE for Pt(111)) is taken from Rizo et al.[18] Solution pH was controlled by $HClO_4$ and KOH so that H^+ and OH^- remain the principal potential determining ions.

As already discussed in the Introduction, Frumkin and collaborators first postulated the relationship between PZFC and potential at which ζ = 0.[40] In absence of ion specific adsorption, these two values should coincide. Here, the potential at which zeta potential is equal to zero, $V_{\zeta=0}$, increases when electrolyte pH increases from 2 to 12. For pH of 2 the $V_{\zeta=0}$ is 0.24 V vs SHE, for pH of 7 it is 0.32 V vs SHE and for pH of 12 it is 0.55 V vs SHE. Rizo et al. measured PZTC of

Pt(111) in 0.1 M $HClO_4$ to be 0.3 V vs SHE for pH 1, and calculated PZFC from there to be 0.28 V vs SHE, and is independent of solution pH[18] when proper adjustment is done. As σ_M is the electronic charge on the metal, this charge should not depend on bulk pH. Frumkin and Petri argued that PZFC can have dependency on pH[12], however this is not supported by more recent works by Feliu and coworkers[18]. The dependence of $V_{\zeta=0}$ on pH may be explained by surface complexes that are present during electrokinetic experiment, but the EDL model considered in this study does not account for them. For example, at pH 2 and $V_{app} \sim$ PZFC, $\sigma_M = 0$, but there are some H_{ad} on Pt forming partial charge and shifting the overall charge on the metal to be slightly positive at $V_{app} \sim$ PZFC. To balance this overall positive charge, σ_d must be negative and $\zeta > 0$. An opposite effect is found at pH 12 where at PZFC, the overall charge on the electrode is negative because of the negative oxide dipole groups at the surface. To balance this overall negative charge, σ_d must be positive and $\zeta < 0$. For pH 7, ionic charging is very low, and as a result, $\zeta \sim 0$ at $V_{app} \sim$ PZFC. Here it is clear that $V_{\zeta=0}$ is not equal to the PZFC because even at PZFC, pH dependent surface adsorption exists which generally makes ζ nonzero at PZFC. The existing model does not account for fractional charges in the form of adsorbed H or oxide species.

Next, the metal charge, σ_M, is plotted as a function of applied potential, V_{app}, as shown by Figure 4(a). Using the data from Figure 3(b), and assuming $\sigma_{IHP} \sim 0$, we get $\sigma_M (V_{app}) = -\sigma_d (V_{app})$ from Eqn. (5). Figure 4(a) shows the monotonic increase in metal charge with applied potentials for all three different pH cases. No metal-charge reversal behavior was observed here, however, σ_M saturated for $V_{app} > 0.7$ V vs SHE to about constant value of 10 $\mu C/cm^2$. Huang et al. developed an EDL model by combining the effects of electrosorption of oxides and potential dependent orientation of water dipoles at the IHP.[11] In that work, σ_M was calculated from σ_{tot} data obtained from CO displacement by Feliu's group.[18] It was found that σ_M first increases with increasing

potential, then decreased and became negative after that. However, no fundamental reason was given to explain this phenomenon. It is well-understood that increasing V_{app} increases the free energy of electrons in the metal atoms. As a result, more metal atoms get oxidized with increasing V_{app}. It is expected that σ_M would increase monotonically with V_{app} unless poly-Pt surface undergoes significant oxidation and cannot be considered as a poly-Pt anymore. This is possible due to place-exchange mechanism of oxygen embedding itself into Pt surface, rendering it to be closer to PtO rather than poly-Pt.[56–58] Traditional CO displacement method fails to produce σ_{tot} data for $V_{app} > 0.74$ V vs SHE for pH 1 because of CO oxidation at these high potential.[59] So, it cannot be used as a probe to measure charge above 0.74 V vs SHE. Feliu's group has developed similar method with peroxydisulfate to understand the PZFC reversal but the results of the experiments, at the time of writing this manuscript, are still not conclusive.[60]

Figure 4(b) shows the ratio of ionic conductivity at the OHP to bulk electrolyte using Eqn. (4). The conductivity ratio plots show near-parabolic profile with applied potential with minimum value of 1. The increased ionic conductivity in the diffuse layer is caused by the presence of higher concentration of ions than the bulk electrolyte. According to Eqn. (4), ionic conductivity in this layer has a minimum where $\zeta=0$. At this minimum, ionic conductivity is equal to the bulk ionic conductivity and the ratio becomes 1. For any other V_{app}, $\zeta \neq 0$ and there is a net charge in the diffuse layer. As a result, ion density in the diffuse layer is more than that in bulk. Ionic conductivity in this layer is also higher. Figure 4(b) shows that the ionic conductivity at the OHP can be as high as 12 times that of bulk electrolyte. As the electrolyte is 0.1 M $KClO_4$ titrated to pH 2, 7 and 12, the bulk ionic conductivity was also high (~1300 mS/m) which is ~2.5×10^5 times the conductivity of deionized ASTM I water. One cannot use the ζ (or σ_d) values directly to estimate this ratio of conductivity with pure DI water as ζ (or σ_d) depends on the background electrolyte.

From the data in Figure 4(b), one can only estimate the OHP conductivity to be orders of magnitude higher than DI water. Note that above $V_{\zeta=0}$ the OHP is populated with negative ions, whereas below $V_{\zeta=0}$ protons are the major current carrying ions.

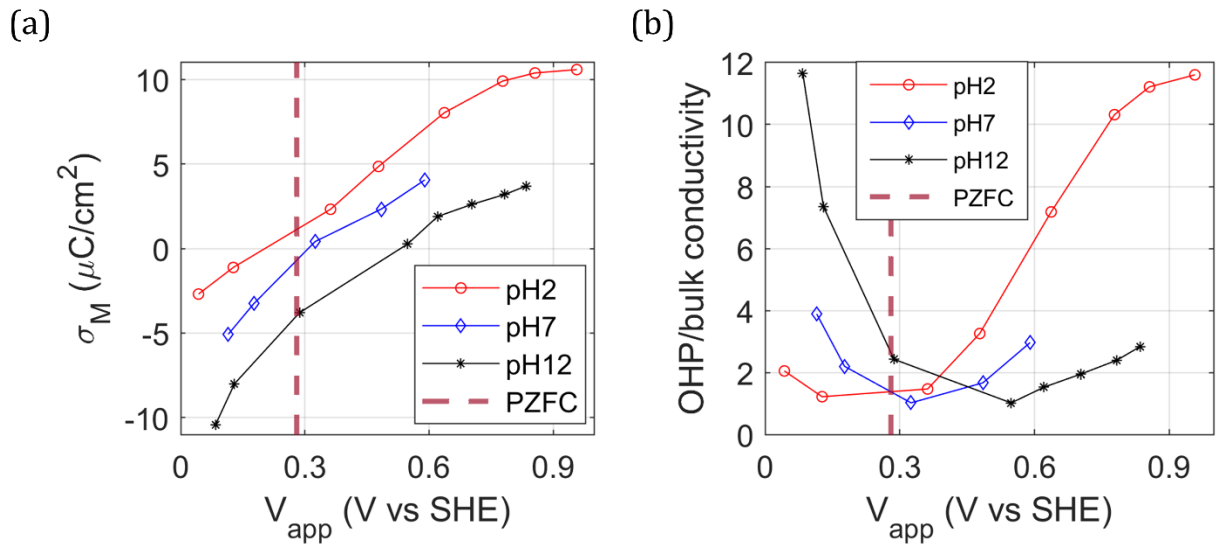

Figure 4: (a)Metal charge σ_M and (b) ratio of ionic conductivity at OHP to bulk as function of V_{app} for 3 pH values (acidic, neutral, and basic) in 0.1 M $KClO_4$ electrolyte. PZFC for Pt(111) is used as a guide and taken from ref.[18]

Lastly, the metal charge, σ_m data obtained with the electrokinetics method in this study is compared to σ_{tot} measured using electrochemical (CO displacement or CV integration) methods. From Eqn. (6), the concentrations of H_{ad}, OH_{ad} and O_{ad} are added to σ_M to estimate the σ_{tot} and compare it with electrochemically measured σ_{tot}. $\Gamma_{Ox} = N_{tot} \times \theta_{Ox}$ where θ_{Ox} is the oxide coverage, which was estimated from the CV of poly-Pt in 0.1 M $KClO_4$ at pH 2. N_{tot} is the density of sites on poly-Pt. Although oxide coverage can be calculated from the CV, H-coverage cannot, as it

consists of underpotential deposited H (H-UPD) and overpotential deposited H (H-OPD).[61] The lower limit of CV was chosen to be above H oxidation potential, so the OPD part cannot be obtained from the CV. $\Gamma_H = N_{tot} \times \theta_H$ where θ_H is the H-coverage estimated from Frumkin adsorption isotherm equations. SM Section S3 contains the detailed method of calculating θ_H, θ_{Ox} and N_{tot} for poly-Pt. The CV is plotted in Figure 5(a) and the coverages are plotted in Figure 5(b). The coverage of oxides is the sum of coverages from OH_{ad} and O_{ad}.

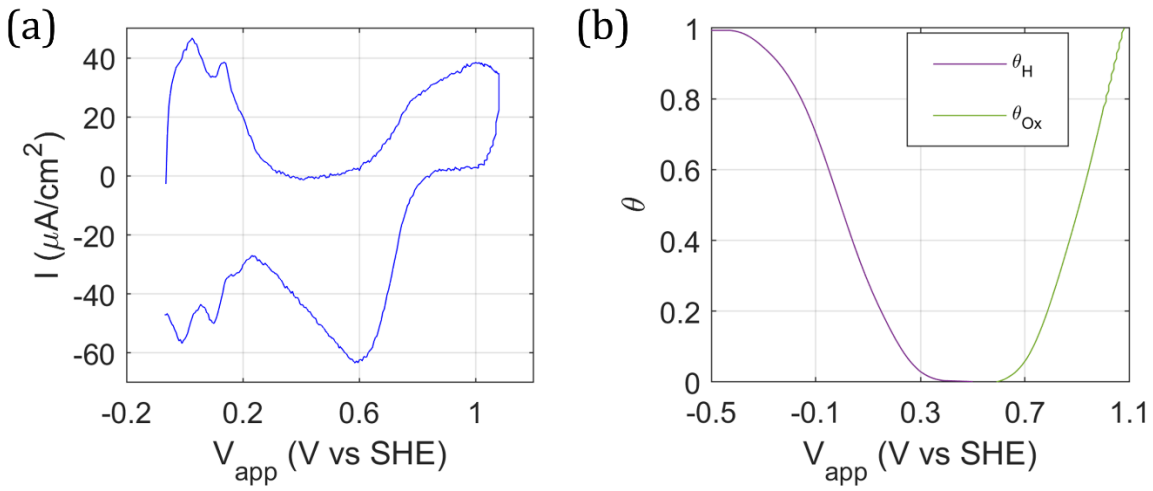

Figure 5: (a) CV of poly-Pt in 0.1 M $KClO_4$ + pH 2 done ex-situ, (b) coverage of chemisorbed H and oxides. H coverage was calculated from Frumkin adsorption isotherm equations for Pt(111), Pt(110) and Pt(100) and then averaged. H coverage included both UPD and OPD. Oxide coverage was calculated from the anodic sweep of the CV shown in (a).

Now, the values of $\sigma_{tot}(V_{app})$ measured using CO displacement method by Feliu's group[18] are compared with the $\sigma_M(V_{app})$ obtained from Figure 4(a) combined with coverage of adsorbed species found from Figure 5(b). The comparison of σ_{tot} as a function of applied potential, obtained

from two methods is plotted in Figure 6(a). A breakdown of the contributions of different chemical species (metal charge, H-coverage and oxide-coverage) is plotted in Figure 6(b). The comparison shown in Figure 6(a) is not very rigorous because Feliu's group used Pt(111) and this study used poly-Pt. Feliu's group used 0.1 M $HClO_4$ as the electrolyte and here 0.1 M $KClO_4$ was used, which was titrated to pH 2 by $HClO_4$. Some deviations due to difference in crystalline structure is expected. Figure 6(a) shows that the magnitude of σ_{tot} measured in this study (poly-Pt) is smaller than that for Pt(111) for a given potential. Pt(111) has the highest electrochemical activity among all the crystal faces of Pt and this is most likely due to this effect. Figure 6(a) also shows an experimental advantage of electrokinetic method over the CO-displacement method in terms of operational potential range. CO oxidation to CO_2 occurs above 0.74 V vs SHE at pH 1.[59] Electrokinetic method can be used safely for $V_{app} > 0.74$ V vs SHE, as it doesn't rely on Faradaic reactions for charge measurement. Figure 6(a) also shows the $\sigma_{tot}(V_{app})$ values calculated using electrokinetic method values for V_{app} > CO oxidation potential. Figure 6(b) shows that at potentials V_{app} > PZC, chemisorbed oxides (OH_{ad} and O_{ad}) contribute most in measured σ_{tot}, while for V_{app} < PZC, H_{ad} contributes mostly in measured σ_{tot}. In the capacitive potential window ($0.35 < V_{app} <$ 0.56 V vs SHE), $\sigma_{tot} \sim \sigma_M$ as the concentrations of chemisorbed species are minimal. Next, the study will be extended to single crystal Pt, specifically Pt(111) to confirm these findings on more controlled Pt surfaces.

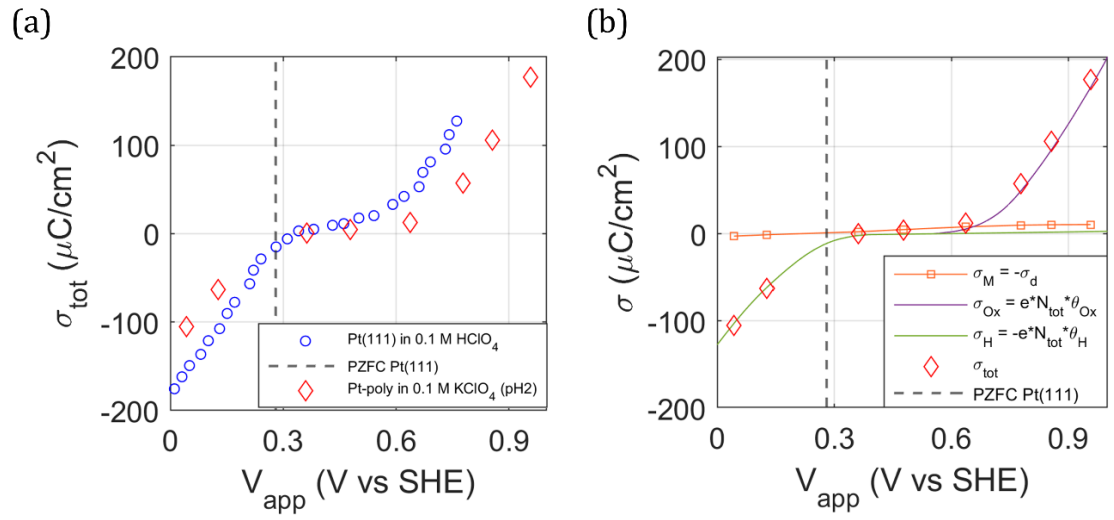

Figure 6: (a) σ_{tot} as calculated from CO displacement for Pt(111)[18] and novel electrochemical-electrokinetic method, (b) Breakdown of contributions from different chemical species to σ_{tot}

Conclusion

A novel electrochemical-electrokinetic method to study interfacial charging behavior at metal-electrolyte EDLs was applied to poly-Pt-electrolyte interface. Precision of electrokinetic methods, especially streaming current, have improved significantly since the time of Frumkin, who studied interfacial charging by the deflection of suspended metal balls and wires in electric field.[30] In this study, perchlorate anion containing electrolyte was chosen to minimize specific adsorption of ions and simplify interpretation of the charging data. Zeta potential (ζ) was measured for different applied potential, V_{app}, and pH of the solution. When no potential was applied on the Pt electrode, i.e., when the electrode was in OCV condition, ζ decreased and diffuse layer charge, σ_d, increased with increasing pH. When V_{app} was applied while measuring streaming current, ζ was found to be monotonically increasing with increasing V_{app}. This indicates that σ_M increases with

increasing V_{app}. Specific adsorption was assumed to be 0 for this study. The applied potential, $V_{\zeta=0}$ at which zeta potential is zero was correlated to PZFC. When surface dipoles were not present significantly (in neutral electrolyte) the $V_{\zeta=0}$ was equal to PZFC of poly-Pt, however in acidic (pH 2) or alkaline (pH 12) electrolytes $V_{\zeta=0}$ deviated from the PZFC, which was reported in earlier studies to be pH-independent.[12] In this study, no metal-charge reversal was observed over the applied potential range up to 0.95 V in acidic electrolyte. However, metal charge saturated to a constant value above 0.7 V vs SHE. A comparison between the σ_{tot} obtained from the electrokinetic method proposed in this study and that measured by CO displacement method from literature was done. The advantage of electrokinetic method is that surface charging can be studied for potentials higher than 0.74 V vs SHE while the CO displacement studies are limited to below that potential. Good agreement was observed between the two methods, providing additional validation of the electrokinetic method. Ionic conductivity in the diffuse layer was calculated from ζ. It was found to be the same as the bulk when ζ=0, and higher for all other applied potentials. In future, this method will be used to study possible charge-reversal on Pt surfaces in presence of poisoning electrolytes due to specific adsorption of anions at potentials higher than known potential of zero charge. A more precise single crystal surfaces will be studied with this method, such as Pt(111). A challenge with this method is that relatively large planar samples are required.

Supporting Information

S1) Experimental method to obtain zeta potential with no applied potential, S2) Experimental setup and equivalent design and procedure to obtain zeta potential, S3) Surface coverage from CV, S4) Zeta potential obtained with electrophoretic light scattering method, S5) Comparison of zeta potential from Figures 2a and 3a.

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Table of Content

Electric Double Layer at Polycrystalline Platinum-Electrolyte Interface Probed By Electrokinetic Streaming Current Method

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